Removal of Heavy Metals from Landfill Fines with Ammonium Citrate in combination with Ultrasound.

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Introduction The cleaning up of historic landfills is a major ecological challenge. In this study a historic landfill site, containing domestic and industrial waste, in the East of Flanders will be excavated. The excavated fines fractions are polluted with heavy metals and have to be cleaned with the intention to reuse them as building materials. However, the cleanup of the investigated fines fraction is insufficient with the conventional soil washing process. A possible improvement can be obtained by using ultrasound combined with chelating additives. Transient low pressure cavitation bubbles formed under the influence of ultrasound can collapse creating an in-rush of the fluid into the void. This in-rush results in micro jets targeted at the surface of the solid particles. These jets can cause: (i) breakup of agglomerates and even particles with an increase of contact surface, (ii) formation of micro pores and little cracks through which the washing liquid can enter the particles, and (iii) increase mass transfer due to the enhanced micro-mixing [1,2] However, as high concentration of metals are leached, re-adsorption also occurs [3]. Chelating additives form metal complexes with the pollutants enhancing the solubility of the metals in the washing solution and preventing re-adsorption on the fines. [4,5,6] Due to its better biodegradability and high leaching efficiency $(NH_4)_2$-citrate was chosen for this application.

Materials and methods Experiments were performed with fines between 80 and 200 µm which were excavated from a landfill for industrial waste in the East of Flanders. The leachability of cadmium and copper exceeds the limit values while the total concentration of cadmium, copper, nickel, lead and zinc in these fines are higher than the prescribed limits. The leaching experiments were carried out in a glass beaker of 1 liter containing 500 ml water and an amount of fines according to the desired L/S-value. For good macromixing an overhead stirrer was also used at 1200 rpm. The experiments with ultrasound were carried out by using a UP200S ultrasonic processor from Hielscher (24 kHz; max. 200 W) with a S14 probe. During treatment, the beaker with solution was cooled in a cold water bath to maintain room temperature. The influence of additive concentration (0; 0.05; 0.1 and 0.2 M $(NH_4)_2$-citrate), pH (3; 7 and 10), liquid over solid ratio (L/S 10 and 5) and ultrasonic energy input (0 and 200W) was investigated. After 60 minutes of treatment samples were taken and analyzed with ICP-MS (X-series1 ICP-MS from Thermo Elemental) to determine the total concentration of the metals in the fines after treatment. To determine the leaching values of the treated fines, the fines were washed three times with water to remove the adsorpted agents on the particles. These agents will enhance the leaching of the metal pollutants.

Results and discussion The influence of ultrasound in combination with complexing agents on the leachability and on the total concentration of heavy metals is displayed in table 1. The influence of ultrasound was investigated by comparing the results of the leaching experiments with ultrasound (24kHz, 200W) and those without ultrasound. Next to the ultrasonic intensity $(NH_4)_2$-citrate concentration (0.05M and 0.1M) was also varied for the washing experiments without ultrasound and with 100% of ultrasound. According to the leaching results shown in table 1, the total concentration of the heavy metals in the fines after extractions with ultrasound are significantly lower than those without ultrasound. When the leaching as well as the total concentration of the metals is taken into account it can be stated that the washing condition with 0.05M $(NH_4)_2$-citrate and 100% of ultrasound is most suitable. This washing procedure results in leaching values beneath the Flemish limit value while for all the other conditions the leaching of copper still exceeds the limit value. This procedure also gives better removal efficiencies than the procedures without ultrasound and gives extraction results comparable to the procedure with the same ultrasound intensity but with the double amount of citrate (only lead gives better results with the latter). The removal efficiencies for this experiment are always higher than the required removal efficiencies for the metals As, Cd, Cr and Zn but did not reach the required removal for the metals Cu, Ni and Pb.

Table 1: Comparison between washing with and without ultrasound.

Ultrasound	***Without***		***100%***		***Flemish limit value***
$(NH_4)_2$-citrate	***0.05 M***	***0.1 M***	***0.05 M***	***0.1 M***	
Leaching of inorganic pollutants (mg/kg DM)					
As	0.029	0.034	0.075	0.087	0.8
Cd	0.018	0.027	0.012	0.007	0.03
Cr	0.456	0.475	0.082	0.111	0.5
Cu	**0.994**	**1.249**	0.125	**0.799**	0.5
Ni	0.276	0.489	0.647	0.453	0.75
Pb	0.657	0.679	0.108	0.115	1.3
Zn	2.311	2.665	1.445	1.530	2.8
Total concentration of inorganic pollutants (mg/kg DM)					
As	2.2	1.6	0.4	0.4	250
Cd	8.2	6.1	0.7	0.6	10
Cr	370	359	340	344	1250
Cu	**799**	**755**	**675**	**828**	375
Ni	**407**	**390**	**352**	**362**	250
Pb	**1558**	**1399**	**1594**	1195	1250
Zn	**1973**	**1381**	141	285	1250

Conclusions A classical washing procedure for solid waste fractions can be improved by using ultrasound waves in combination with $(NH_4)_2$-citrate. The improved procedure consists of one extraction step and three washing steps. The extraction step was carried out by using a $(NH_4)_2$-citrate concentration of 0.1M and 40W of ultrasonic power (24 kHz) at L/S = 10 for 1 h. The use of this technique results in a significant reduction of the total concentration of the regulated metals in the ELFM fines. Only the concentrations of copper, nickel and lead exceeds the Flemish limits while the leaching ability for all the regulated metals is lower than the limit value.

References

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